

ENVIRONMENTAL SCIENCE AND TECHNOLOGY DIVISION
FY00 Technical Progress Report
for April, 2000

CLEAN WATER TEAM

Team Leader: Terry Ackman

Ground-truthing and Characterizing Targets Identified by Remote Sensing (Veloski, Sams, Dotson):

Developed GIS procedures for processing thermal data in the Sewickley Creek basin. Each data point represents a thermal anomaly that was identified using remote sensing software. The end products of GIS data processing is an Arcview shapefile in polygon format, which is used to represent the extent of the thermal feature, and an Arc point coverage, which is used to represent the centroid of the feature. An Arc/Info AML program was designed to efficiently process this data. After processing the data through GIS software Arc/Arcview, each data point is attributed with the following information: Project_id, Area, Latitude, Longitude, Temperature Code, Line Number, Group_id, Type (Site Description), Groundwater Code (Potential Site). The attribute for Groundwater Code is a yes or no value used to distinguish between potential groundwater discharge sites and cultural features such as building vent pipes. A USGS Digital Ortho Quad is used as a background for this determination. With this information, specific sites can be selected for display and data analysis.

Most of the potential water pollution sites detected in the aerial remote sensing infrared data acquired in the Sewickley Creek Watershed have been incorporated into a geographical information systems database coverages. These coverages have unique identifiers assigned to them, and carry with them a number of unique database fields, including: the geographical position in decimal degrees, U.S. Geological Survey quadrangle location, flight line number, watershed boundary and whether or not this feature is a member of a group of related features. In addition to this tabular data, the visual database incorporates a grayscale representation of the original flight line images, U.S. Geological Survey digital quarter quadrangles, U.S. Geological Survey 7.5' contoured quadrangle maps, location of coal seams/outcrops, digitized and georeferenced mine maps, surface streams, and 30m digitized topography. In addition, the user may select to view the original polygons shapefile coverages or point objects representing the geographical centroid of all selected thermal anomalies. The geographical positions for each of the thermal anomalies can be uploaded to the handheld GPS units. Printed maps are currently being generated for anticipated preliminary field activities that will focus on the groundtruthing of thermal anomalies extracted from the GIS database. Efforts are also underway to acquire property maps from local municipalities. Digitized property boundaries will be incorporated into the database as overlays. It will be absolutely necessary to establish contact with landowners before engaging in field exercises.

The Muddy/Roaring Creek watersheds, Winding Ridge and Kempton sites thermal flight line data are currently being processed to warp the imagery using manually selected ground control points to

conform to high accuracy aerial photographic maps. These data will then be classified and further processed in a fashion similar to the Sewickley Creek data.

Several members of the Clean Water Team attended a U.S. Geological Survey course in Denver during the week of April 3-7, on Introduction to Geophysics for Hydrological and Environmental Studies. The course provided an overview of geophysical methods and their appropriate applications. One day of the week long course was spent in the field for hands-on use of equipment. The instructors provided a wealth of reference materials to supplement their lectures. This training will be useful for understanding geophysical data being used for current watershed assessment projects.

Geophysical Surveys at Montana Mines--The preliminary results from geophysical surveys conducted at two mine sites in Montana were presented to EPA and MSE in Cincinnati. This work was funded by EPA and carried out in conjunction with MSE as part of their mine remediation program.

The Miller Mine is an abandoned underground gold mine that is the source of water with high metals content. The remediation strategy was to determine areas where groundwater was entering the mine and inject those areas with grout. This action was expected to limit the amount of water entering the mine and thereby, reduce the contaminant load being discharged. Geophysics was employed to delineate areas of water-filled fractures, the potential conduits for water entering the mine. VLF surveys were conducted both within the mine and on the ground surface above the mine. Because VLF anomalies can arise from mineralized zones as well as water-filled fractures, a gradient magnetic survey was also conducted that responds to mineralization but not to water. Therefore, a comparison of VLF and magnetometer results can eliminate non-water anomalies. A target area that was identified by geophysics was subsequently drilled and grouted by MSE. Flow and water chemistry data are currently being collected to determine the effectiveness of grouting.

VLF surveys were also conducted over waste rock dumps at the Peerless Mine, an abandoned silver and base metal mine. The purpose of these surveys was to identify water-filled fracture zones that may underlie the dumps, paths of water flow through the dumps, and perched water tables within the dumps. The results of these surveys were contradictory and cannot be explained without additional work.

Remote Sensing Work in California--NETL is currently collaborating with EPA in Cincinnati regarding the potential application of remote sensing technologies to the Clear Lake - Sulfur Banks Superfund site in California. NETL has generated the scope of work for EPA. A contractor from EPA Region 9 will pursue the contracting of the remote sensing work. NETL will receive the remote sensing data from the vendors conducting the airborne surveys and will interpret the data, generate a GIS data base, and conduct land-based geophysical investigations to confirm interpretations, and write the final report.

Passive Treatment of Mine Drainage (Watzlaf & Schroeder):

George presented an invited presentation - "Overview of Passive Treatment Technology and Performance of the Jennings Vertical Flow System at the Slippery Rock Watershed Coalition 2000

Symposium, April 6-7, 2000, at the Jennings Environmental Center near Slippery Rock, PA.

The final camera-ready copy of the paper "Long-Term Performance of Alkalinity-Producing Passive Systems for the Treatment of Mine Drainage" by G. R. Watzlaf, K. T. Schroeder, and C. Kairies has been submitted for the 17th Annual American Society for Surface Mining and Reclamation Meeting, June 11-15, 2000, in Tampa, Florida.

Watershed Remediation (Ackman, Schroeder, & Hammack):

Laboratory analyses of the samples obtained during the trip to Lorberry Creek, Swatara Watershed, Pennsylvania on March 13 were received on 04/06/00. A second trip to the watershed took place during the week of April 10. Preliminary analysis of the March 13 data indicate that approximately 15 mg/L alkalinity (as CaCO₃) needs to be added to Lorberry Creek to increase the pH to the 7.0 region. At this pH, the iron will oxidize with a half-life of about 36 minutes. Assuming the iron concentration will not exceed the historical high of 15 ppm, 3 half-lives (108 min) will meet effluent standards of 3 ppm and 4 half-lives (145 min) will reduce the levels to below 1 ppm. It was found that the oxidation can be accelerated using KMnO₄ and presumably other oxidants would work too. Oxidation in the presence of KMnO₄ was so fast that the rate could not be measured. Settling of the fine iron (oxy)hydroxide remains a problem at this site. During the trip of the week of April 10, attempts were made to settle the iron more rapidly by introducing an anionic flocculating agent. The laboratory analyses of the samples generated were not received as of the end of the month.

Colloidal Sludge Characterization and Utilization (Hesbach & Lamey):

Minor revisions have been completed in the Sludge Volume Reduction paper, and additional supporting references have been found and added prior to submittal for NETL approval. The literature search continues on the mortar and grout applications of ash and AMD sludge. Conversations with personnel in the EAO Division provided information regarding formal testing of grouts and mortars. Preliminary formulations have been made containing FBC ashes alone with water; FBC ash, fly ash, sludge, and water; and a baseline mix of FBC ash, fly ash, water, and a trace of cement.

Water sampling continued at the Omega mine site as part of the continuing assessment of water quality. The on-going work at this site by WV DEP to modify the water seepage collection system and by their contractors to relieve blockages combines with precipitation events to produce wide monthly variation in flows measured at specific sampling points.

Regional Standardization of Watershed Characterization Procedures for Volunteer Watershed Groups (Ackman & Harrison):

NETL, in cooperation with the U.S. EPA, held a multi-agency meeting on Thursday, April 20, 2000 to discuss standardization and classification of watershed assessment practices on a regional basis. The objective of this standardization and classification effort is to provide added confidence in collected data and promote a holistic watershed approach so that better management and funding decisions can be made in the future. The product of this effort will be training video tapes that will

be available in both VHS and internet formats, as well as a hard copy document.

The initial meeting was attended by the USGS, WV DEP, EPA. Presentations were provided by both NETL and WV DEP. The concept for the standardization of characterization procedures for watersheds, and ultimately, generating a one-stop shopping approach amongst Federal and State agencies was well received by the attending group. The group agreed that a video approach was a good idea and well worth pursuing and identified several video topics. However, prior to pursuing topical videos it was decided that a master educational video, which would lay the foundation (why, when, how, etc) for subsequent videos, will be pursued first.

It is anticipated that the resultant videos will be the first of perhaps a series of such products. Furthermore, it is anticipated that the participating agencies can be linked together through the internet so that all of our products can be more broadly accessed.

Use of a Novel Polymeric Additive to Stimulate the Microbial Sequestration of Heavy Metals in Contaminated Soils and Sediments (Edenborn & Brickett):

Vibrio fischeri bacteria were incorporated into 2% low-temperature gelling agarose and were poured into sediment gel probes. The probes were incubated in solutions containing 0, 25, 50, and 100 ppm zinc for 1 h. After this time, triplicate 3 cm gel sections were excised from each probe and the total light emitted was integrated using the luminometer. A linear response of light emission from the gels was observed (ca. 8, 4, 2, and 0.1 relative light units (RLU)). Light emission was too low to be detected after relatively short exposure times (ca. 15 minutes) by the CCD camera/chemiluminescence system. This may be due to the low bacterial cell density in the gels or less than optimum detection settings using the chemiluminescence system.

Experiments carried out with MitoScan submitochondrial particles showed that sensor development may be possible using this toxicity system. The mitochondria contain enzymes that mediate the reactions that supply the vast majority of cellular energy obtained from the oxidation of glucose and tricarboxylic acid (TCA) cycle intermediates. The mitochondrial particles are sensitive to toxicants that block or damage one or more of these enzymes as well as those toxicants that may disrupt membrane, membrane-protein, and protein-protein interactions. Agarose gel probes were incubated in copper-containing solutions for 1 hour, followed by a second equilibration period for sliced sections in deionized water. These solutions were tested using the submitochondrial toxicity method (specifically the electron transfer protocol (ETr)), in which NADH is added as an activator to start the reaction and the rate of disappearance of NADH is monitored spectrophotometrically as it is oxidized to NAD⁺. The decrease in absorbance is measured at 340 nm at timed intervals to obtain the rate of reaction. The ETr protocol is sensitive to toxicants that inhibit Complex I, Coenzyme Q, Complex III, Cytochrome c and Complex IV of the electron transport system. Inhibition was detected using this "secondary equilibration gel probe method," suggesting that the approach should be applicable as a way to measure the vertical distribution of toxic substances within sediment porewaters.

A novel application of the automated spiral plater to determine sediment porewater concentrations of sulfide was tested by applying known sulfide-containing solutions to copper-containing agar

plates. The spiral plater can dispense decreasing volumes of solution on an agar plate as the plate spins and the unit moves a liquid-dispensing stylus from the the interior of the plate to the outer edges. A three-order magnitude dilution in concentration occurs on a single plate. In this experiment, deposited sulfide solution instantly precipitated with copper in the agar and formed a black spiral image that could be photographed and analyzed digitally. It is expected that this method may permit the rapid quantification of sulfide on small volumes of sediment porewater, as well as other analyses based on similar precipitation or colorimetric reactions.

Development of Novel Biosensors for the Detection of Environmental Contaminants (Edenborn & Brickett):

Amendments were added to aliquots of metal-contaminated soil taken from a zinc smelter site. Three different polylactic acid polymer amendmets were tested (high percent residual lactide/low molecular weight (fine and coarse grind), and high percent residual lactide/high molecular weight), sodium lactate solution, glass beads, polycaprolactone, and chitin. These were added with or without gypsum as an added sulfate source, as well as water, and were placed in a constant temperature incubator. These will be monitored for the effects of added amendmets on conditions reflective of bacterial sulfate reduction activity (increased pH, decreased Eh, increased acid-volatile sulfide concentration), and finally analyzed for the partitioning of heavy metals via sequential extraction procedures.

In collaboration with the U.S. EPA, sites were identified in Alabama with mercury-contaminated soil that may be candidates for the polymer amendment approach of remediation. Efforts are currently underway to identify potential obstacles to working with the materials on site.

Biodegradable polymer amendmets were placed in open-ended buckets in the sediment of a SAPS (sequential alkalinity producing system) system in Clarion County, PA. Amendmets included 3 different polylactic acid polymer formulations, polycaprolactone (PCL), biodegradable garbage bags (consisting of PCL and corn starch), as well as spent mushroom compost. Granulated limestone was also added as an amendment to each treatment, but this appeared to dissolve immediately, as the current pH of the surface water at this site is ca. 3.0. The low pH also had a negative effect on the biodegradable bags, apparently reacting with alkaline materials in the bags to form small gas bubbles, which increased the buoyancy of the material. The amendmets will be left in place until the late summer, when sediment cores will be taken, subsampled, and evaluated for signs of polymer stimulation of bacterial sulfate reduction activity.

Lab experiments examining various amendmets to sediments from the SAPS site discussed above were continued. After 8 weeks, the greatest amount of bacterial sulfate reduction (reflected in increased pH, decreased Eh, increased acid-volatile sulfide concentration, and increased numbers of sulfate-reducing bacteria) had occurred in sediments receiving biodegradable bags composed of polycaprolactone and corn starch. Polylactic acid polymers also stimulated bacterial activity, with low molecular weight and high percent residual lactide polymer providing the most rapid response. Polyglycerol lactate did not stimulate bacterial sulfate reduction activity and had the lowest pH and most oxidizing conditions after 8 weeks incubation. Limestone addition appears to have facilitated the onset of sulfate reduction in initially acidic samples, but has a lesser impact on net sulfate

reduction activity over time.

Solid Waste Management Team

Team Leader: Ann Kim

Regulatory Determination on Wastes from the Combustion of Fossil Fuels:

On April 25, 2000, EPA issued a regulatory determination for “fossil fuel combustion wastes” generated as co-managed wastes. Earlier in the year, under pressure from environmental groups, they had proposed to regulate fossil fuel wastes as a tailored *Subtitle C* (hazardous) material, specifically when used in mine backfill. DOE, OSM and others argued that any classification of coal combustion by-products as hazardous would significantly curtail all beneficial uses of this material and that there was no evidence that CCBs caused damage to health or the environment. Data from the Solid Waste Team’s laboratory and field studies was submitted in support of this position. EPA did conclude that CCBs should generally not be regulated under subtitle C. The following material is a brief summary of EPA’s 68 page regulatory determination.

EPA has determined that fossil fuel wastes do not warrant regulation under Subtitle C of RCRA and is retaining the hazardous waste exemption under RCRA Section 3001 (b) (3) (C). However, they also determined that national regulations under *Subtitle D* of RCRA are warranted for coal combustion wastes when they are disposed in landfills or surface impoundments, and that regulations under *Subtitle D* of RCRA (and/or possibly modifications to existing regulations established under authority of the Surface Mining Control and Reclamation Act (SMCRA)) are warranted when these wastes are used to fill surface or underground mines. So that coal combustion wastes are consistently regulated across all waste management scenarios, they also intend to make these national regulations for disposal in surface impoundments and landfills and minefilling applicable to large volume coal combustion wastes that had been exempted under the 1993 regulatory determination. EPA concluded that no additional regulations are warranted for coal combustion wastes that are used beneficially (other than for minefilling), and it does not wish to place any unnecessary barriers on the beneficial use of fossil fuel combustion wastes so that they can be used in applications that conserve natural resources and reduce disposal costs.

For minefilling, although EPA is concerned about placement directly into groundwater, they have not yet identified a case where placement of coal wastes can be determined to have actually caused damage to ground water. In addition, the federal regulatory program under SMCRA is expressly designed to address environmental risks associated with coal mines. Industry, academic, state agency, and federal agency commenters encouraged EPA not to adopt national regulations or voluntary restrictions on minefilling because: (a) nationwide standards would not be conducive to the site-specific evaluations needed to appropriately control these operations; (b) minefilling creates no adverse environmental impacts and EPA identified no damage cases associated with this practice; (c) existing state and federal regulatory programs and industry practices are sufficient to control any risks from this practice, and (d) federal standards would be an unreasonable interference with state authorities. Additionally, several industry representatives, legislators, and state mining and

environmental agencies mentioned that this practice, when used to remediate abandoned mine lands, will produce considerably greater environmental benefits than risks. Further, minefilling is a relatively inexpensive means to stop or even reverse the environmental damage caused by old mining practices, and through remediation by minefilling, these lands frequently can be returned to productive use. These commenters recommended no additional regulation of this practice. However, public interest groups have insisted that minefilling should be regulated under RCRA *Subtitle C* or prohibited due to potential impacts on potable water sources even though there is no evidence that such damage has ever occurred. Therefore, EPA generally encourages the practice of remediating mine lands with coal combustion wastes when minefilling is conducted properly and when there is adequate oversight of the remediation activities. EPA expects that *Subtitle D* controls, or upgraded SMCRA controls or a combination of the two, should provide sufficient clarity and incentive to ensure proper handling of this waste when minefilled.

Phosphate Remediation with FBC Ash *Principal Investigators: Kim and Dahlberg*

Laboratory tests have indicated that the addition of 25 % by volume of coal combustion by-products (CCBs), from either conventional boilers or FBC units, to phosphate slurries does not improve the settling characteristics. Rather, the fly ash becomes evenly dispersed within the slurry. The unamended slurry contains between 80 and 93 pct moisture. At ratios greater than 3:1 for the slurry and fly ash, the mixed material contains between 69 and 80 pct moisture. This material remains plastic unless dried at 105 ° C. Preliminary tests of mixtures with between 35 and 50 pct fly ash by volume indicate that at these lower ratios of slurry to CCB, a self-hardening material is formed. Future experiments will focus on mixtures within this range of concentrations.

Under a University Partnership, a student from the University of Pittsburgh, Rob Cimaroli, has completed a literature review of the factors that control dispersion of the clay particles in the phosphate slurry.

Capping Sediments *Principal Investigators: Brickett and Edenborn*

Work continued on the manuscript, "The Use of Coal Combustion By-Products for Sub-aqueous Capping of Contaminated Sediments," by H. Edenborn and L. Brickett for the Journal of Water, Air and Soil Pollution.

Poultry Waste Stabilization *Principal Investigators: Brickett and Kim*

An experiment was conducted to determine how much phosphate and nitrate are released from five chicken waste samples (#31, #23, AR, CE, PEL). Two-gram samples of the manures were digested using two different leachate solutions, distilled water and 1% H₂SO₄/ 30% H₂O₂. The distilled water was used to determine minimal leaching quantities while the acid leachate served to define maximum leachable quantities. Samples were analyzed using three analytical techniques to compare the results, and to determine which technique would be used for future experimental analysis. Total phosphorous concentration was determined by I.C.P., and phosphate was analyzed by L.C. Total nitrogen was analyzed by Kjeldahl, and nitrate was analyzed by L.C. The results indicated that four of the samples were very similar in phosphorous and nitrogen content. The pelletized sample, which

is known to release less phosphorous than unpelletized wastes, did contain 50% less phosphorous. However, it released much more nitrate than the unpelletized samples. Due to the different nature of the pelletized sample, future work will not include this sample.

Analytical results indicated that the water leached approximately 50% of the total nitrogen when compared to the nitrogen from the acid leach, and between 20 and 40% of the total phosphorous when compared to the phosphorous from the acid leach. When total phosphorous concentration analyzed by I.C.P. was compared to phosphate analyzed by L.C., the majority of phosphorous was in the phosphate form. In contrast, the majority of nitrogen was in forms other than nitrate. Since the objective of the project is to determine if the addition of fly ash will slow the release of phosphorous and nitrogen from chicken waste, the total concentrations of these elements and the speciation are critical values.

CCB Leaching *Principal Investigators: Kazonich and Kim*

The fly ash leaching test (FA 38, 39, 40, and 41) was completed by the end of April. All fly ash samples were leached until acidified with the acetic acid to between pH 3 and 4. This has been used as a testing end point since alkaline fly ash samples begin to release most of their toxic metals when leachates reach about pH 5. The concentration of metals in the leachate peaks shortly after neutralization and then makes a slow decline over time. The duration for the last test was 60 days for the most alkaline fly ash samples (FA39 and 41). The Solid Waste Team has processed all leachate samples and will transport the few remaining samples to the water lab for analyses when refrigerated storage space is available. The final analyses for tests FA38 through F41 should be received this month, since the lab is currently running about a month behind. Volume and pH data have been added to the computer data files of this test up to March 8, 2000.

Preparations for the next set of tests has begun. New columns have been fabricated through the in-house contractor. Some FBC fly ash samples have been requested from a regional utility working with DOE, but may not be available. Conventional flyash samples and samples of FGD sludge have been offered by regional utilities and will be picked up this month in preparation for a start up at the end of May or the beginning of June.

Both EPA and the Clean Air Division have expressed interest in the Solid Waste Team's capacity to perform comprehensive leaching tests on fly ash, particularly with respect to the release of mercury. The leaching system will also be used to determine the rate of release of phosphorous and nitrogen from the chicken waste/fly ash mixtures and from the phosphate slurry amended with fly ash.

PA DATA *Principal Investigators: Cardone and Kim*

A paper entitled "Water Quality Changes Related to Mine Placement of Coal Combustion By-Products" has been selected for presentation in the technical sessions at the Annual Conference of the Association of AML Programs. This conference will be held in Steamboat Springs, Co. in September. The paper will evaluate the effects of CCBs on water quality based on the results from individual mines sites in Pennsylvania using the PA DEP database.

The PA Department of Environmental Protection is in the process of developing an information reporting system call eFACTS (Environment, Facility, Application, Compliance Tracking System). NETL was able to extract useful information on the effect of fly ash on ground and surface water in the vicinity of surface mines where ash had been placed in backfills. This apparently demonstrated to PA DEP that their permitting and monitoring data was useful to regulators and to the environmental community, but it needed to be more accessible. The new system will take 2 years to implement but will allow easy access to programs and information on permitting data by facility, site, owner, county or watershed association.

L. Brickett, C. Cardone, G. Kazonich and A. Kim attended the OSMRE Technical Interactive Forum: The Use and Disposal of Coal Combustion By-Products at Mines, April 11-12, 2000 at NETL Morgantown. The following poster presentations highlighted the Solid Waste Team's program:

1. Assessment of Coal Combustion By-Products and Water Quality Variations at Mine Sites.
2. Mine Remediation with Coal Combustion By-Products
3. The Release of Common Metals from Fly Ash During Leaching with Low pH Liquids

Innovative Technologies Team

Team Leader: Duane H. Smith

QUANTITATIVE, PREDICTIVE MODELING OF WATERSHEDS AND RESERVOIR GEOLOGY

Quantitative Prediction of Reservoir Boundaries (Smith and Edwards):

We have completed a fully nonlinear modal analysis of river meandering and have submitted a manuscript to Physical Review Letters on the subject. This analysis relies on the Ikeda, Parker, and Sawai model of river meandering supplemented by our new dynamical equations governing river migration and length. The analysis identifies a critical centerline wave number for river meandering that separates long-wavelength bends, which grow to cutoff, from short-wavelength bends, which decay. Although the analysis predicts the usual downvalley migration for small-amplitude bends, it also predicts upvalley migration for very large-amplitude bends which precede oxbow cutoff, where adjacent bends meet. Together with a peak in the cross-valley migration rate at intermediate times, this upvalley migration awaits experimental confirmation. We are preparing three other manuscripts on this work.

Numerical Modeling of Flow and Sediment Transport in Rivers (Smith and Ahmadi)

Most of a rather extensive report has been completed, but further computations are in progress.

NATURAL GAS AND NATURAL GAS HYDRATES:

Wellbore and Seafloor Stability in Gas Hydrates (Smith and Siriwardane)

Duane Smith met Bill Durham of LLNL during their meeting at ORNL to discuss a possible joint

proposal of several of the national labs to the BAA. We are arranging a visit to CRREL and USGS (Woods Hole) to organize the measurement of constitutive properties for the seafloor modeling. Seismic data and the choice of seafloor sites also will be discussed at USGS.

Production of Natural Gas Associated with Hydrates

Preparation, and Characterization of Gas Hydrates (Smith and Seshadri)--The preparation and characterization of propane and carbon dioxide hydrates in silica gel of average pore diameters 150 Å, 100 Å, 60 Å and, 40Å were completed. For the preparation of the two hydrates in 40 Å silica gel, 254 K was selected as the formation temperature. The equilibrium pressure-temperature data for the dissociation of propane hydrate displayed two phase changes; one at 249.50 K and the second at 253.00 K. For carbon dioxide, the two phase changes were observed at 250.00 K and at 262.00 K. Therefore, the melting point of ice in the pores of 40 Å silica gel was taken to be near 250.00 K. The phase change corresponding to the second inflection point is yet to be identified.

The fusion temperatures of ice in the four silica gel samples varied linearly with inverse nominal pore diameter with the intercept at 273 K. Encouraged by this result, calculations were completed to estimate the hydrate-water interfacial energy using the equilibrium pressure-temperature data for propane hydrate in all the silica gel samples of different pore diameters. Apparently, the interfacial energy is a function of pore diameter and temperature. In this calculation, density of the hydrate was used and this was obtained using the program developed by Colorado School of Mines..

Equilibrium Pressure-Temperature data were obtained for propane in 100 Å silica gel without any pore water and, the results were compared with analogous data for bulk propane and for propane hydrate. The equilibrium pressure for the pore propane was less than that for the bulk propane and higher than for the pore hydrate. These experiments are useful in understanding the phase changes during the dissociation of pore hydrates.

The data to calculate the heat of dissociation of propane hydrate were consolidated and an equation was obtained relating logarithm of the fugacity with the reciprocal nominal pore diameter and temperature. Using this equation , it may be possible to explain the curvature in the equilibrium pressure-temperature curve for the dissociation of gas hydrates.

Formation and Dissociation Kinetics of Methane Gas Hydrates Smith, H.O.Kono, A. Miller, S.Narasimhan and F.Song--Methane hydrate was synthesized in a custom built high pressure packed bed reactor under the following operating conditions:

- a) Starting Pressure: 130 and 70 atm , Temperature: 273 K
- b) Material of construction of reactor: Carbon Steel
- c) Piping Material: Stainless Steel

The formation rate of the methane gas hydrate was measured in the constant volume reactor. The change of pressure of the reactor was monitored as a function of time. The formation reaction time was varied in the range of 24 ~ 144 hours, while the permeability the methane hydrate was measured and controlled.

Dissociation of the methane gas hydrate was carried out by the method of rapid depressurization from 130 atm down to 10 atm. The amount of gas evolved during dissociation was measured using a flowmeter prepared in the lab.

Dr. Aubrey Miller and Rahul Shukla completed set up for the experiment to be conducted with a Berea sandstone section, except for the coreholder, which is being fabricated. They are currently working on the Data Acquisition System to be used to monitor and record real-time temperature and pressure changes.

Computer Modeling Activities (Dean, Smith, and Ahmadi)

Mara is running the one-dimensional analytical model for production of hydrate natural gas by depressurization and performing parametric studies. She also has initiated a literature review to determine the approach(es) taken by others in their stochastic modeling activities.

Hydrates Thermophysical Properties Project (Ramer and Shaw)

Dave Shaw has used the transient planar source instrument to study the thermophysical properties of water and ice. Some improvements in the data analysis were made as a result of problems that appeared in this first attempt to use the instrument at other than ambient temperatures. However, the results do not agree very well with literature values. More work is being done on calibrating the temperature/resistance response of the nickel strip heater (thermal source) and the effective geometry of the source.

Natural Gas Exploration and Production Product Team Activities (Smith)

The Natural Gas Supply & Storage Product Team has changed its name to the Natural Gas Exploration and Production Product Team. Duane Smith attended a meeting at ORNL to discuss a possible joint proposal of several of the national labs in response to the natural gas hydrates BAA. He is scheduled to continue his series of technical presentations to the Product Team at the meeting in May, speaking on "Quantitative Prediction of Reservoir Boundaries."

GLOBAL CARBON CYCLE:

Mara continued writing the Implementation Plan for the CO₂ focus area - work will continue in May, with a much better understanding of the total CO₂ effort, the NETL's role, and the in-house portion of activities. Mara will begin frequent interaction with Bob Warzinsky in May to avoid duplication of efforts.

CO₂ Capture Processes for Mitigating Global Climate Change (Siriwardane, Poston, and Smith)

The preprint on capture by physical adsorption for the American Chemical Society meeting in August was written and submitted. Duane Smith attended the presentation on capture and sequestration of the year-long senior design project in chemical engineering at WVU and discussed the results with the students and Prof. Turton.

Sequestration of CO₂ In Coal Seams, And Production Of Methane Therefrom (Jones, Smith, and Ahmadi):

Funds have been transferred to support a University Partnership student to model gas flows through fractured porous media (i.e., coal seams and their cleats). A SARS package has been written for the experiments.

Sequestration of CO₂ By Injection into Deep Formations Saturated with Brine and Depleted-Oil (Ramer, Smith, Ferer, and Ogunsola):

An abstract was submitted and accepted for the national meeting of the American Chemical Society in Washington, DC in August. The Fuel Division preprint also was written. Grant Bromhal has submitted an application for an NRC Associateship to begin in September to perform modeling for this project.

Three-Dimensional Imaging Support for Geological Sequestration of CO₂ (Ramer and Smith):

Considerable information has been collected on commercial instruments and academic installations. The DOE's Carbon Sequestration roadmapping paper was used to identify critical OST needs in the area of three-dimensional imaging. Work needs to be done on an equivalent study of OST needs related to natural gas production and storage.

EFFICIENT COAL UTILIZATION:

Ash Management Project (Ramer)

Soon Kweon, a CMU graduate student, continues to make progress in learning image analysis techniques. He is currently analyzing ash deposits collected at two different operating temperatures, with the objective of quantifying the visually observed differences in particle size and particle volume fraction. The second week in May, Everett Ramer will attend the Engineering Foundation Conference on ash management.

Characterization of Coal for Advanced Combustion Applications (Ramer)

Parsons has completed the leaching and ICP analysis steps of the chemical fractionation analysis of seven candidate coals for the Lakeland CCT Project. Ash analysis is currently being done on the solid residues from the leaching.

Hot-Gas Filtration (Smith, Seshadri, Ferer, and Ahmadi)

At the request of Southern Services, several reprints were sent to them for use at the Wilsonville facility. Their intent is to use the model described and tested in these publications to perform online

estimates of thickness and other important filter-cake properties.

Development of Evolved Gas Analysis Technique for Predicting Environmental Consequences of Mining (R. W. Hammack)

Twelve years ago, research by current NETL employees showed that the evolved gas analysis (EGA) of coal mine overburden samples had potential for predicting the environment consequences of mining. Although the EGA technique had distinct advantages over other overburden analysis methods, the new technique suffered from instrument limitations that were difficult to overcome. Since that time, technology advancement has eliminated these problems. In FY 99 and FY00, EGA has been reevaluated for overburden analysis by ViRoLac Industries under contract to NETL. Results of this evaluation showed that EGA still offers unique performance advantages over conventional methods of overburden analysis, albeit at a slightly higher cost.

The result of this work was presented at:

Acid Base Accounting Data Determined for Mine Overburden by Programmed Temperature Oxidation by Robert LaCount, Richard W. Hammack, and Douglas Kern presented at PittCon 2000, New Orleans, LA, March 12-18, 2000.

Improving the Acid-Base Account using Programmed Temperature Oxidation and Evolved Gas Analysis by Douglas Kern, Robert LaCount, and Richard Hammack, presented at the Annual Meeting of the Acid Mine Drainage Task Force, Morgantown, WV, April 4-5, 2000.

Biological Flue Gas Cleanup (R. W. Hammack)

The SO_x/NO_x analyzer system has been purchased and should be delivered in 2-3 weeks. When the final cost of the SO_x/NO_x analyzer is known, it will be possible to determine if enough project funds remain to move the pilot plant from building 21 to building 94. The compilation of the construction/operational SARS package for relocating the pilot plant is currently underway.

A CRADA concept statement (CCS) was prepared for a proposed CRADA between NETL and Paques, B. V. This CCS has been signed by Robert Romanoski, the product manager, and is awaiting Rita Bajura's signature.